Long-Term Fate of Depleted Uranium at Aberdeen and Yuma Proving Grounds Final Report, Phase I: Geochemical Transport and Modeling

M. H. Ebinger
E. H. Essington
E. S. Gladney
B. D. Newman
C. L. Reynolds

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CONTENTS

FIGURES

TABLES

LONG-TERM FATE OF DEPLETED URANIUM AT ABERDEEN AND YUMA PROVING GROUNDS FINAL REPORT, PHASE I: GEOCHEMICAL TRANSPORT AND MODELING

by

M. H. Ebinger, E. H. Essington, E. S. Gladney, B. D. Newman, and C. L. Reynolds

ABSTRACT

The environmental fate of fragments of depleted uranium (DU) penetrators in soils and waters at Aberdeen Proving Ground (APG) and Yuma Proving Ground (YPG) is a concern to the Testing and Evaluation Command (TECOM) of the U. S. Army. This report presents the information from preliminary soil and water samples that were collected from the humid woodlands of APG and the arid Sonoran Desert of YPG. Soil samples collected beneath a penetrator fragment on the firing range at APG showed approximately 12% DU by weight in the surface horizon and DU significantly above background to a depth of about 20 cm. Samples of surface water at APG showed U only at background levels, and bottom sediments showed background U levels but with isotopic ratios of DU instead of natural U. Soil samples beneath a penetrator fragment at YPG showed about 0.5% by weight U in the surface horizon, but only background concentrations and isotopic ratios of U between 8 and 20 cm depth. Results from this preliminary study indicate that DU at APG was redistributed primarily by dissolution and transport with water and possibly by migration of DU colloids or DU attached to small particles. Redistribution at YPG, however, was mainly due to erosion of DU fragments from the impact area and redeposition in washes that drain the area. Proposed work for FY90-FY92 includes additional field sampling, laboratory column studies, and the development of a computer model of DU redistribution at both sites.

I. INTRODUCTION

Depleted uranium (DU) and DU alloys are used in a variety of applications, including munitions, by all branches of the military. Extensive testing of DU munitions has occurred at several locations in the U.S., leading in some cases to large inventories of DU in target areas, soils, and the immediate surrounding environment. Of fundamental interest is how DU can be transported out of the munitions impact areas and whether transported levels of U could harm the environment and/or man.

This report summarizes the results of a study conducted by Los Alamos National Laboratory for the Testing and Evaluation Command (TECOM) of the U.S. Army at Aberdeen Proving Ground (APG) on Chesapeake Bay in Maryland and at Yuma Proving Ground (YPG) in the Sonoran Desert of Arizona. The purpose of the study was to collect and compare information on the physical and chemical relationships that control the distribution and transport of DU in these two contrasting environments. Results of the study will be used to focus future effort on technical information needs that are relevant to site assessment activities at each location.

The strategy for developing this program stems from the regulatory requirement to characterize contaminated sites and to conduct a health risk assessment based upon the site characterization data. Depending on the outcome of the site assessment, site remediation may or may not be required. A general schematic of the process (Figure 1) emphasizes the importance of having good information on the physical, chemical, and biological relationships that govern the fate of DU in the environment and, by extension, govern the risks and control measures available to limit exposures to organisms including man. Two fundamental questions that must be answered in order to complete site characterization and site assessment activities are:

- how is the DU distributed in the physical (soil, water) and biological components of the environment? and

- how is it being transported?

The primary focus of the Los Alamos work at APG and YPG is on measuring and modeling of DU transport with particular emphasis on hydrologic and chemical transport processes.

Colleagues at Pacific Northwest Laboratory (PNL) (Erikson et al. 1989; Nelson and Price 1989; Price 1989; Stoezel et al. 1985) are focusing on the

2

distribution of DU in soils, water, and biota at APG. We have agreed to share data to avoid duplication of effort and reduce program costs.

Interest in the environmental fate and effects of expended DU munitions dates back at least 15 years (Hanson 1974; Hanson et al. 1974) when studies on the distribution and transport DU began for the U.S. Air Force in the firing areas at Los Alamos National Laboratory. A variety of studies have been conducted since 1974 (Hanson and Miera 1976, 1977, 1978; White et al. 1979, 1980; Elder and Tinkle 1980; Rodgers et al. 1984, and Scripsick et al. 1985). Pertinent results from this early work will be discussed later in this report.

II. METHODS AND MATERIALS

A. Sampling Methods

A limited number of soil, water, and sediment samples were collected at several locations within and outside penetrator impact areas at APG and YPG to establish horizontal and vertical relationships of DU and natural uranium in soil and to estimate the role of surface water and sediments in accumulating and/or transporting DU. Information on sampling locations is summarized in Table 1 and Figures 2 and 3.

Soil samples in impact areas were intentionally collected from beneath penetrator fragments to provide unambiguous data on the vertical distribution of DU. Background soil sampling locations outside the impact areas were selected to provide estimates of natural uranium concentrations and isotopic ratios. Vertical samples were taken at given depths by excavating small pits to expose the soil profiles. Samples were taken from given depths from a freshly scraped portion of the wall to minimize possible cross-contamination of profile samples. All samples were sieved to remove particles >2 mm and then air dried before analysis for uranium.

Surface water at APG was collected in 4.5-L containers and sequentially passed through 0.45-μm and 0.05-μm membrane filters. Filtered water was analyzed for pH, dissolved oxygen (DO), total alkalinity and total conductivity within 24 hours of collection. Subsamples of the filtered water were also analyzed later for cations, anions, and uranium.

Well water (Well H) was sampled at YPG because permanent surface water does not exist. The well was pumped until chloride, added as chlorine to purify the water, was below the detection limits of a field test kit. Sample

preparation was analogous to that for water samples at APG.

Grab samples of bottom sediments from stream and pond water sampling locations at APG were air dried, sieved to remove the >2 mm fraction, and analyzed for uranium.

The $^{235}U/^{238}U$ ratio determined from total U in a sample gives information on the source of U in the sample. U from natural sources (UO_2, etc.) has a $^{235}U/^{238}U$ ratio of 0.0075 (±0.00075) whereas U from DU penetrators has a $^{235}U/^{236}U$ of 0.0020 (±0.00020). Since these ratios are significantly different, the source of U in a sample from APG or YPG can be identified. Results presented below show that both natural U and U from DU penetrators were found at APG and YPG, depending on whether the sample was from a background location or from a penetrator impact location. In addition, the $^{235}U/^{238}U$ can confirm or refute the selection of a sample as a representative background sample. This ratio is a sensitive tool for the determination of the source of U in a sample.

B.   Analytical Methods

The pH of water samples was measured with an Orion pH meter using standard glass and/or combination electrodes calibrated against buffers of pH 4.0 and pH 9.0. Dissolved oxygen was measured with a YSI Model 57 DO meter and corrected for the altitude of the analytical location. Total alkalinity was determined by titration (Hem 1989; Rhoades 1982), and electrical conductivity was measured with a digital conductivity meter calibrated against 0.01 N KCl (Rhoades 1982). Each analysis was completed within 24 hours of sampling to minimize chemical change after sampling.

Several analytical methods were used to measure the chemical parameters reported in this study. Anionic species (F^-, Cl^-, N as NO_3^-, SO_4^{2-}, and P as PO_4^{3-}) were determined via ion chromatography. Cation species (Ca^{2+}, Na^+, K^+, Mg^{2+}, Fe^{2+}, Si^{4+}) were measured using inductively coupled plasma atomic emission spectrometry (Gautier and Gladney 1986). Total uranium in soil and sediment samples was determined using delayed neutron assay (Perrin and Gladney 1982; Conrad et al. 1982), and depleted uranium was measured by instrumental epithermal neutron activation analysis (Gladney et al. 1978; Gladney et al. 1979; Gladney et al. 1980). Uranium isotope ratios were measured using inductively coupled plasma mass spectrometry on uranium separated from the samples of interest (Gladney et al. 1989; Gladney et al.

4

1983). Quality assurance was provided on all analyses by the concurrent analysis of certified reference materials using the acceptance criteria documented by Gautier et al. (1988).

III. RESULTS AND DISCUSSION

A. Water Samples, Filters, and Sediment

1. APG. The results of cation, anion, pH, DO, and U analyses for the water samples from APG are given in Table 2, and sample locations are shown in Figure 2. Samples from Mosquito Creek (AW-1) and Romney Creek (AW-2) were chemically similar except for higher Si at Mosquito Creek and higher Fe at Romney Creek. Sample AW-3 showed the influence of mixing the fresh water of Mosquito Creek and the brackish water of Chesapeake Bay, in that most cations and anions were higher than the other water samples from APG, with large increases in Na^-, Cl^-, SO_4^{2-}, and higher pH (7.04). The sample from the swamp/pond (AW-4) exhibited the lowest concentrations of basic cations (i.e., Ca^{2+}, Mg^{2+}) and an intermediate concentration of SO_4^{2-} that may indicate the presence of HS^- or H_2S.

Direct measurement of Eh (i.e., measurements with Pt electrode) were not made because these measurements are often misleading and may not reflect the oxidation potential of a given system accurately (Lindberg and Runnels 1984). Instead, dissolved oxygen (DO) was measured within 24 h and Eh was calculated from the concentration of DO in the water samples. Eh values calculated from the DO measured from each water sample indicated oxidizing conditions at the time of sampling and ranged from 700 mV to 900 mV. The Fe^{2+}/Fe^{3+} couple was also measured in order to calculate a second value of Eh for the water samples. The results however, were inconclusive because sufficient Fe^{2+} to calculate the ratio was not detected, possibly due to the 24-h delay between sampling and analysis. Results of total organic carbon (TCC) analyses showed that the Mosquito Creek sample (AW-1) was the lowest of the range for the APG waters of 7 mg/L to 20 mg/L.

Total U analyses were conducted on each water sample, but all results were below the detection limit of 1 ppb (1 μg U/L water). Because of the low U concentration in water, isotopic data could not be obtained. The concentration of U trapped on the 0.45-μm and 0.05-μm filters (in ng U/L water that passed through the filters) is given in Table 3. Figure 4 shows more U

5

was trapped on the 0.45-μm filter and that the sites within the firing range showed the highest U concentrations in this fraction. These results cannot be fully interpreted, however, because data on the background concentration of U from the material retained by filters were not collected.

Chemical equilibrium calculations suggest that the APG water samples are saturated with respect to the layer silicates kaolinite and smectite, quartz and other silicate phases, and iron oxides (e.g., goethite). These results were expected, because the water was probably in contact with the local soils and the water composition was derived from the soils. The presence of the minerals listed above in soils at APG was qualitatively verified during the soil sampling and when the soils were sieved before chemical analysis.

The total U concentrations in sediment samples (Table 4) from Mosquito Creek (AD-1 and AD-3) and from the swamp on the firing range (AD-4) were at background levels (AD-2). The isotopic ratios, however, suggest that U from DU penetrators was present in Mosquito Creek and firing-range sediment samples.

2. YPG. The results of cation, anion, pH, DC, and U analyses for the water samples from YPG are given in Table 2. The YPG water sample was typical of a Na-Ca-Cl groundwater from a deep aquifer in the western United States (Winograd and Robertson 1982) except for high F$^-$ concentration. Previous data on water samples at YPG also show high F$^-$ (P. Saunders, personal communication), possibly indicating contact with fluorite or other fluorine-containing minerals in the aquifer.

Calculated Eh ranged from 700 to 900 mV due to the DO in the sample. The Fe^{2+}/Fe^{3+} couple was not measured, so no comparison of Eh calculated from two redox couples was made. The TOC result (24 mg/L) was surprisingly higher than the TOC at APG. We can not explain this apparent anomaly at this time except that analytical inaccuracy is probable. Total U and U isotope data were not obtained from this sample because total U was below the detection limit. Total U trapped on the 0.45-μm and 0.05-μm filters was low and probably reflects background U concentrations, but data on background concentrations were not collected for these size fractions.

B. Soil Samples

1. APG. Soils unaffected by anthropogenic sources such as additions of U from DU should reflect the average abundance of U in the earth's crust of 2-

4 ppm and $^{235}U/^{238}U$ ratio of 0.0075. Total U concentrations in the "background" sample (AS-1, Table 4) were near background at levels of 2-4 ppm. Isotope ratios suggest, however, that horizon AS-1A (0-5 cm) and horizon AS-1C (15-23 cm) contained some U from a DU penetrator, whereas U from horizon AS-1B was characteristic of natural U. These results require us to choose a different "background" site and resample in order to estimate background U levels in APG soils.

Soil samples from locations AS-2 and AS-3 (Figure 2) contained as much as 4% and 12% total U by weight, respectively, due to their close proximity to penetrator fragments. Recall that a DU penetrator fragment was found on top of the soil profile sampled at location AS-3 (Table 1). Total U concentration in the 0-5 cm (AS-3A) horizon was 115,000 ppm and decreased exponentially to about 30 ppm in the 15-20 cm (AS-3B) horizon in the AS-3 profile (Figure 5). Thus, while soils attenuated a large portion of the U that was removed from the penetrator, there was some transport through the soil column. Note that the isotopic ratios of U in AS-3 carried the DU signature (Table 4). Total U concentrations were lower at location AS-2, and also reflected the isotopic ratio of DU. Depth sampling at location AS-2 was not done because the penetrator fragment was buried vertically in the soil, potentially contaminating several horizons.

2. YPG. Concentrations of U and isotopic ratios for samples collected at YPG (Figure 3) are given in Table 5. Samples were collected from distinct soil horizons identified after a shallow pit was dug in the soils of interest. The profile samples collected at location YS-1 were representative of background (2-4 ppm U) based on the total U and isotope ratios. Samples at location YS-2 were collected in the dry stream channel adjacent to the "hill and berm" impact area to determine whether transport of U by erosion had occurred. Concentrations of uranium in the two profile samples averaged from 5-10 times background and did not decrease sharply with depth, possibly reflecting the turbulent mixing of sediments that occurs during rainfall runoff events in ephemeral streams in the Southwest.

The profile at location YS-3 was in an upland area covered by a relatively stable surface feature of cobbles and gravel also known as desert pavement. The sample was taken from beneath an obvious yellow stain at the surface of the desert pavement. The yellow material was later identified by x-ray diffraction as schoepite $(UO_2(OH)_2 \cdot H_2O)$. Elevated U concentrations from

DU were found in the 0-1 cm (YS-3A) horizon and 1-8 cm (US-3B) horizon of the profile. The lowest horizon sampled (8-20 cm), however, showed only background U concentration and only natural U isotopic ratios (Figure 6).

IV. RESULTS OF MODEL CALCULATIONS

A. Chemical Equilibrium Model

Equilibrium calculations were made with the EQ3/6 code (Wolery 1983) to illustrate the relationships between dissolution of DU and formation of soluble and insoluble species as a function of the composition of the water. The reaction progress variable, ξ, in Figures 7-9, is the logarithm of the number of moles of DU that dissolved; the reaction is complete and the calculation ends when all DU has dissolved.

In an ideal system containing pure water, DU dissolves slowly (Figure 7) because there are no soluble species (i.e., species of Si or Al) available to form complexes with U. Precipitation of schoepite begins early, but the rate of precipitation is slow because there are no competing reactions in the system. In contrast, calculations with APG and YPG water compositions show increased rates of DU dissolution, increased rates of insoluble schoepite formation, and later formation of schoepite because significant concentrations of soluble species are found in these waters. The soluble species present in water at APG or YPG sequester U and other constituents, resulting in faster dissolution of DU and different precipitation mechanisms than in pure water. Calculations were made with water composition data of pure water and natural water from APG and YPG to test the methods of the calculations and to contrast the rates of the DU dissolution reactions in water of different compositions for later laboratory studies.

Schoepite, identified in samples from YPG, was the least soluble mineral under the conditions of the calculations (high Eh). Formation of other U-containing precipitates (i.e., U_3O_8, UO_2) is possible, but these solids are unstable and were omitted from Figures 7-9 for clarity. The dissolution of the layer silicate, kaolinite, and precipitation of gibbsite ($Al(OH)_3$) in Figures 8 and 9 illustrate that other minerals react in the same manner as DU and schoepite when water compositions from APG and YPG are used in the calculations. Thus, dissolution and precipitation of uranium in natural surface and groundwater can be complex.

8

The calculations and evidence from the field suggest that the alteration of DU penetrators to soluble U occurs, but formation of several secondary minerals is possible. In environments of high oxidation potential (high Eh), schoepite is one of the favored secondary minerals. Formation of schoepite as DU dissolves from a penetrator limits the total concentration of U to about 10^{-5} M. Thus, most of the U from a penetrator remains in a solid phase while some is available for transport. Soluble U could be transported by solution through soil or water, but will be retarded by interaction with the medium through which it moves. Adsorption of U species onto iron and manganese oxides and layer silicates (clays), complexation of U by organic matter, uptake by plant roots, and precipitation of additional secondary phases may retard the transport of U and decrease the total U in solution even further. Eventually, total U in solution may be controlled by a secondary phase such as tyuyamunite ($Ca(UO_2)_2(VO_4)_2$) or carnotite ($K_2(UO_2)_2(VO_4)_2$), both of which are more stable than schoepite (Erikson et al. 1989). Control of U by these phases was not modeled because we did not have the required thermodynamic data. If tyuyamunite and/or carnotite form in soils as DU dissolves, only small amounts of U (10^{-8} M or less) would be in solution. These minerals were not found in the soils from APG or YPG, but chemical conditions are favorable for their formation in APG soils. A source of V (vanadium) is required to form tyuyamunite and carnotite, but Griffen et al. (1989) suggest that relatively large natural V concentrations are found in Chesapeake Bay area soils. Concentrations of V large enough to suggest the formation of tyuyamunite are also expected in groundwater from western states as a result of contact between groundwater and rocks that contain trace amounts of V.

In environments of low oxidation potential (low Eh), DU is oxidized to secondary phases such as uraninite (UO_2), and total U in solution is considerably lower than U in higher Eh systems due to the increased stability of uraninite. Data of Erikson et al. (1989) and Langmuir (1978) show the low solubility of uraninite relative to tyuyamunite (Figure 10), demonstrating that total U in solution is several orders of magnitude lower in systems with lower oxidation potential. Low oxidation potential is achieved in soils when sufficient organic matter exists to stimulate microbial metabolism, when water tables rise and remain high for part of a year or a season, or when significant concentrations of reduced state minerals (e.g., $FeCO_3$) exist. Organic matter acts as a source of chemical energy for microbes, and oxidation

9

of organic matter releases electrons to the system. Oxygen ($O_2(g)$) is used by microorganisms during respiration and metabolism of organic matter and thus ceases to be the acceptor of electrons as the microbial activity continues. As a result, trace metals are reduced as they accept electrons. Rising water tables also deplete $O_2(g)$, and electrons released during microbial oxidation of organic matter again are accepted by trace metals. For example, an elevated water table in the spring due to runoff could reduce Mn(IV) minerals to Mn(II) minerals as the Mn(IV) minerals accept electrons from the microbial oxidation of organic matter. Later, Mn(II) minerals become unstable when the water table falls and the system re-oxygenates and solid Mn(IV) concretions form. Evidence for this cycle was found in the soil profiles at APG. Presence of reduced minerals (e.g., FeS_2 or $FeCO_3$) may also poise or control a system at low oxidation potential as these minerals weather to more stable minerals. The oxidation of H_2S to SO_4^{2-} could keep the oxidation potential at low Eh in swampy areas and also decrease the solubility of DU in these areas. Direct measurement of soil Eh is of arguable value because Eh is related to specific reactions. The soil profiles, however, showed the formation of Mn oxide concretions and gray areas or mottles that indicate alternating high and low oxidation potential at different times of the year. Thus, Eh varies with time at APG and reducing environments can be expected during part of the year. The results of the U solubility calculations in this report and solubility data presented elsewhere [e.g., Langmuir (1978)] will be used in transport calculations to show possible effects of U movement through time and space.

The chemical equilibrium calculations suggest that DU could dissolve and form secondary solid minerals (e.g., schoepite) as well as soluble species. The amount of U in solution and the kind of solid phases formed depend on the environment. Low Eh due to high groundwater level and/or increased microbial activity in soils could keep soluble U concentration low. Higher Eh due to presence of large concentrations of DO would change the kinds of solid phases that could form and increase the U concentration considerably. The chemical equilibrium calculations not only suggest the U concentrations in solutions and the type of secondary solid phases that could form, but also show the influence of the environment on DU transformation of other solids and soluble species.

B. _Transport Calculations_

Transport of constituents in saturated, porous media such as soils can be modeled using relatively simple computer codes. The equation for one-dimensional transport is given by van Genuchten and Alves (1982) and Javandel et al. (1984):

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial t} - J = R \frac{\partial c}{\partial t} \qquad (1)$$

where D is the dispersivity (m^2/d), which was arbitrarily taken as 10 m^2/d, v is the water flow velocity through the soil (m/d) and was set at 1 m/d, C is concentration of U (M), J is a term that accounts for precipitation or radioactive decay of the material, R is the retardation factor, t is time (d), and x is distance (m) from the input location.

The model was used to estimate the change in U concentration with time at an arbitrary distance of 100 m when D - 10 m^2/d, v = 1 m/d, and J = 0. Initial U concentration was set at 10^{-8} M to represent the background U concentration. The input U concentration was 0.1 M and was injected as a "slug", that is, the U entered the soil over a short time and was transported accordingly. The retardation factor, R, was varied so that the effects of R on transport could be observed. Values of R > 1 indicate that the transport of solutes is retarded with respect to the water velocity because of sorption or other processes, but does not indicate what processes were responsible. Thus, large values of R increase the time for U to travel a given distance. The computer program LINDSOL was developed from a solution to Equation (1) given by van Genuchten and Alves (1982) and was used for the calculations in this report. Calculations of U concentration at 100 m over 1000 d were made.

Results of the calculations of U transport are shown in Figure 11. The U concentration vs. time at an arbitrary distance of 100 m from the U source is plotted for R = 1, 10, and 100. This range of R was selected because the R for APG and YPG soils is not known, so a range of conservative values was selected. Also, data of Hsi and Langmuir (1985) suggest that R for Fe oxides is >100, so the range of R in these calculations probably overestimates the

travel time through the soils of interest because APG and YPG soils had iron oxides present, possibly in large amounts.

For 0.1 M U input over one day and R − 1 (*i.e.*, U moves at the same rate as water), Figure 11 shows that the maximum U concentration at 100 m is observed less than 60 d after injection. Thus, U travels from the injection point to the observation point quickly, then decreases to background U concentration within about 700 days. The same calculation when R − 10 predicts that the peak U concentration will occur at about 600 d. At R − 100, no change in U concentration at 100 m was observed after 1000 d and levels did not reach a maximum until 10,000 d (27 years). The influence of the value for the retardation factor (R) on transport of uranium dictates that good estimates of retardation, as well as other terms in Equation 1, must be available to reliably predict subsurface transport of U from DU penetrators.

C.   U in Soils and Water at Los Alamos

While this report presents the results of Phase I sampling at APG and YPG, pertinent work on U in soils and water has been done at Los Alamos National Laboratory since about 1974 (Hanson 1974; Hanson and Miera 1976, 1977, 1978; White *et al.* 1979; White *et al.* 1980). Elevated concentrations of U from DU in soils and water were measured, the result of about 40 years of dynamic testing activities. Hanson and Miera (1976) suggest that vertical distribution of DU at the dynamic testing sites is due to erosion or subsurface deposition of DU during explosive testing. Rodgers and Cokal (1985, unpublished data) show that the soluble U concentration in soils increased significantly as a result of snowmelt infiltrating into these soils, and uptake of soluble U by the native plants is suggested as a possible concentrating mechanism of U in plants and mammals (Hanson and Miera, 1977, 1978).

Hanson *et al.* (1974) and work of Rodgers and Cokal (1985, unpublished data) show that the particle size distribution of DU fragments dispersed during dynamic testing activities varies considerably. These data suggest that similar considerations are important to assess the solubility of DU particles in soils and water as well as the erodibility of the DU from impact areas. The former consideration will be important at APG whereas the latter

12

will be important to the determination of amount and distribution of DU that can be eroded at YPG.

White *et al.* (1979) reported the development of a sensitive, portable detector for U analysis in the field. This detector can be carried in a backpack, and could prove extremely useful for assessing DU in soils over large areas where collection and analysis of large numbers of soil samples is impractical and/or not economical. For example, this detector could be useful in determining U in the sediments of the dry wash that drains the impact area at YPG sampled in Phase I.

While not entirely analogous to the APG and YPG DU study, the studies at Los Alamos show that soluble U transport and transport by erosion are factors important to DU redistribution in semiarid climates.

V. CONCLUSIONS

A. *APG Samples*

Results of field sampling in Phase I show that up to 12% by weight of U from DU penetrators was found in soils immediately below two distinct penetrator impacts. The U concentration in profile AS-3 decreased with depth, but was significantly above background and retained the DU isotopic signature at 15-20 cm depth. Results based on these limited data suggest that U dissolves from DU penetrators and moves through the soil in association with water. Water samples from the B-3 range and surrounding areas had U concentrations below the analytical detection limit (1 ppb) and yielded no information on the isotope ratio of U. Particles $>0.45-\mu m$ that were filtered from the water sampled on the B-3 range contained elevated U concentrations compared to the water samples from surface water sources away from the B-3 range. The lack of isotopic data, however, precludes attribution of the U from the B-3 water samples to DU. U concentrations in bottom sediments were at background, but isotopic ratios suggest that the U was from DU penetrators in samples from the B-3 range (AD-1, AD-4) or that drained the B-3 range (AD-3). The control sediment sample had only background U concentration and an isotope ratio indicative of natural U. Our limited sampling at APG suggests that solution transport of U is possible and may predominate over erosional transport.

13

B.   YPG Samples

Maximum U in YPG soils was about 0.5% by weight immediately below a penetrator fragment, and decreased to background levels between 8 and 20 cm below the soil surface. The U in the lowest horizon of the profile on the Kofa Range (YS-3) was due only to natural U, not U from DU penetrators. This result suggests that transport of U via solution is of lower magnitude at YPG because of the dry conditions. Soil samples in the wash that drained the impact area showed U concentrations significantly higher than background levels and isotopic ratios indicative of U from penetrators. U concentrations in channel sediments decreased only slightly with depth, possibly reflecting the turbulent mixing of sediments that occurs during storm runoff events in the southwestern United States. Erosion of soil and sediments is likely an important factor in the transport of U at YPG. Transport via solution, however, has not been adequately evaluated, particularly for long time scales.

C.   Chemical Modeling

Results of the chemical equilibrium calculations indicate that DU exposed to APG and YPG waters is soluble and could oxidize to more stable phases over time, but the soluble U concentration and the solid phases that form depend on the chemical environment. Total U in solution is low (10^{-12} M) in systems with low Eh (low oxidizing potential) due to the stability of uraninite (UO_2) or other U(IV) solids. U concentration is higher (10^{-8}-10^{-5} M) in systems with higher Eh (higher oxidation potential) because U(VI) phases (e.g., tyuyamunite, schoepite) are more soluble. Modeling results show that significant U transport by solution could occur at APG and YPG under certain conditions. Data on Eh of the soils at APG and YPG are required to provide a better assessment of the potential for chemical transport.

D.   Transport Calculations

One-dimensional calculations of U transport through soils shows the importance of the retardation factor, R, on U transport. The calculations were made largely with assumed values of key parameters, emphasizing the need to quantify these parameters in future studies. The calculations show that large retardation factors could increase the time of U transport over a 100 m

14

distance to hundreds of years, but small retardation factors result in large U concentrations after only a few days.

E.   Recommendations for Further Study

The limited data and results from Phase I sampling suggest that the factors involved in the distribution and transport of U at APG and YPG are significantly different. Assessment of the potential impact of U on the environment at APG and YPG, as well as possible remediation options, depend on accurately understanding the factors that influence chemical distribution and transport at both locations.

At APG, the limited data suggest that chemical distribution of U from DU penetrators is the major means of U transport. Further studies will address the dissolution of DU penetrators and subsequent redistribution due to movement of soluble species with water. In addition, formation of solid U phases (e.g., schoepite) in soils will be examined more closely as will factors of organic U complexes that could influence the movement of U and the role of adsorption of U onto different minerals in the APG soils. This information will lead to a better assessment of the subsurface migration when coupled with the hydogeologic information that will be available through the environmental monitoring program (Price, 1989). Ultimately, chemical and hydrogeologic information will be used to predict the potential redistribution of U in soils, groundwater, and surface water at APG.

The Phase I data show that the chemical distribution of U at YPG may not be as important as at APG because of the dry conditions at YPG. Surface transport of U, however, is an important factor at YPG, and those factors that influence the amount of U that could be transported away from the impact area will be studied in more detail. Factors such as the particle size distribution of the U on the surface of the impact area and the amount and particle size distribution of U eroding off the impact area will be investigated, as will the vertical and horizontal distribution of U in the wash that drains the impact area. Chemical redistribution at YPG will be considered even though the effects are probably small. This effort will estimate the amount of U that could be in soil solution and a potential impact on the YPG environment.

Further study at APG and YPG may indicate that remediation of either or both sites is required to maintain compliance with different environmental regulations. Several remediation options (*e.g.*, Nyhan 1989) can be considered at the appropriate time and can be designed to decrease U redistribution at either site. Possible remediation, however, will be considered only after adequate information from APG and YPG has been obtained and predictions about U transport and redistribution have been made.

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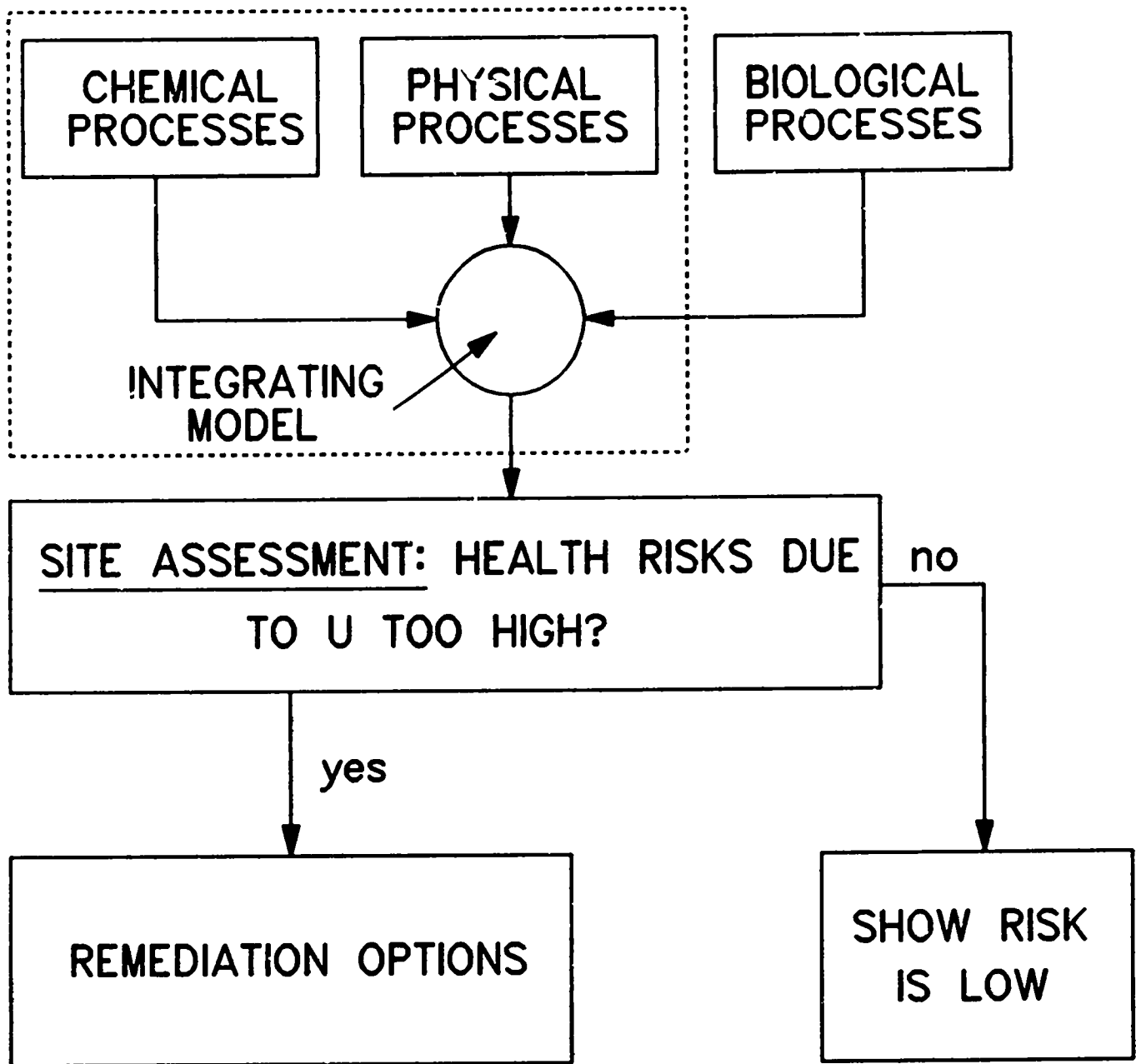   Lawrence Livermore National Laboratory Report UCRL-53414.

Figure 1. Schematic of information needs and integration of information for site assessment.
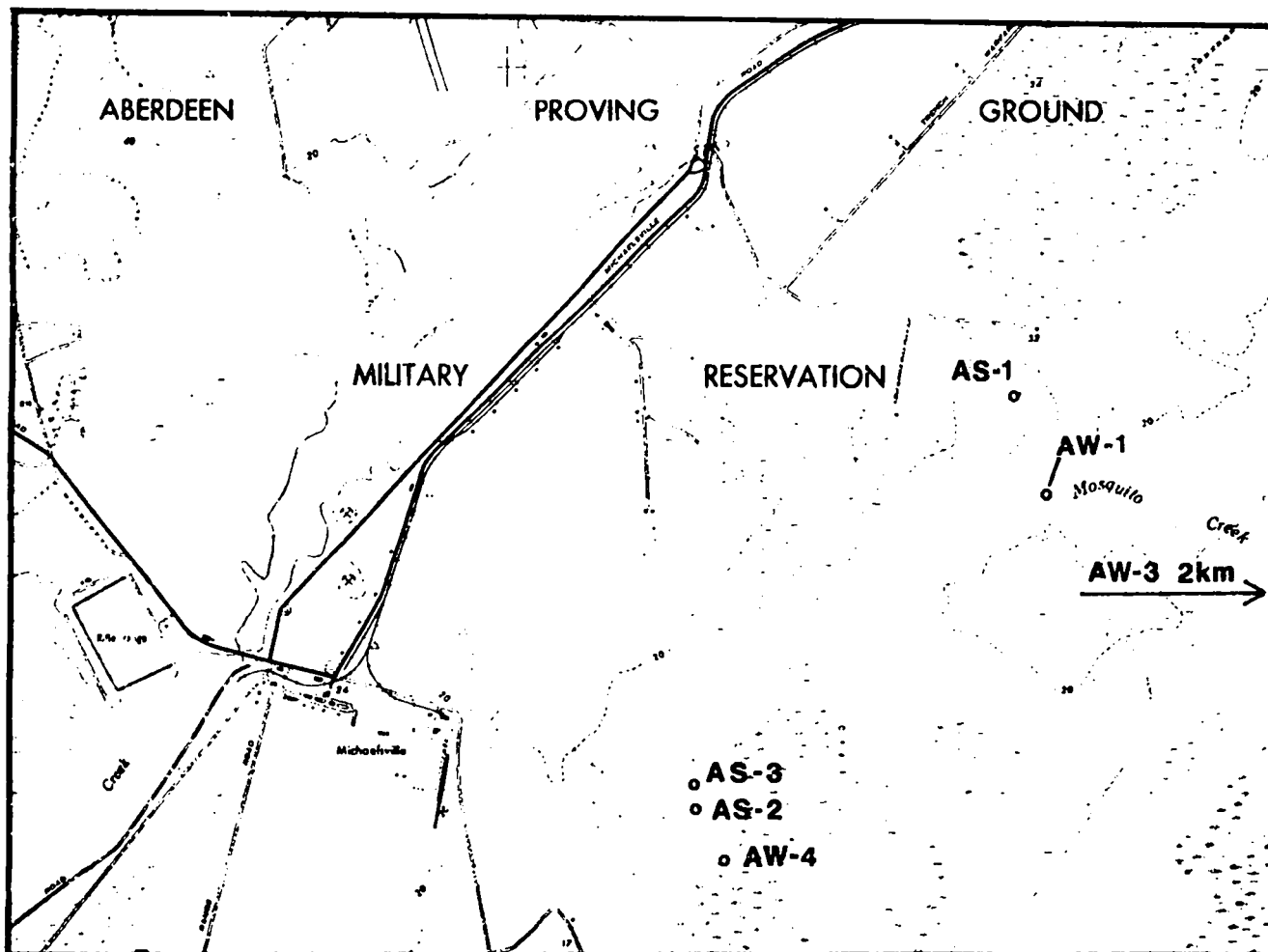
21

Figure 2A. Map of soil, water, and sediment sampling locations on range B-3, APG.
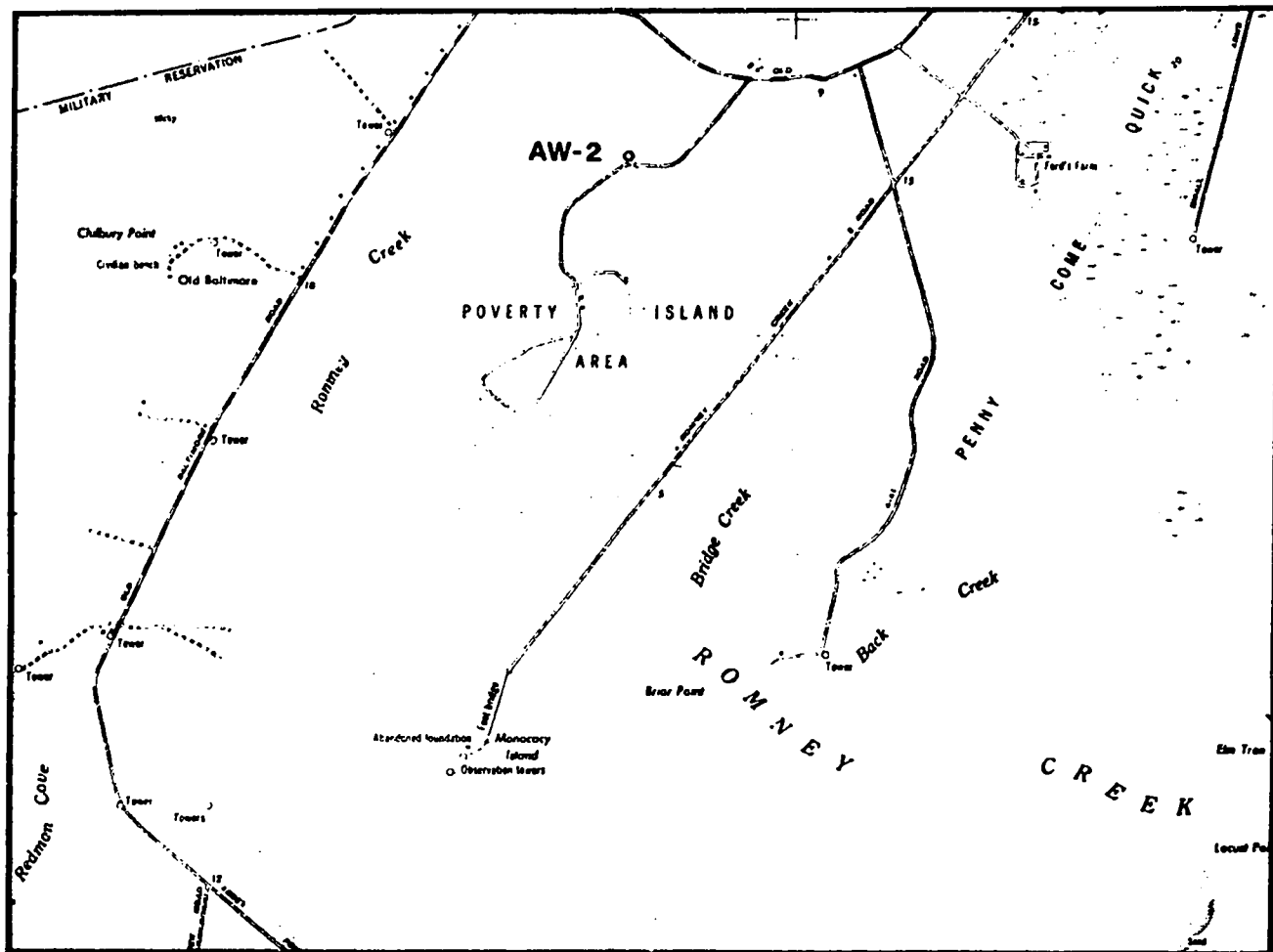
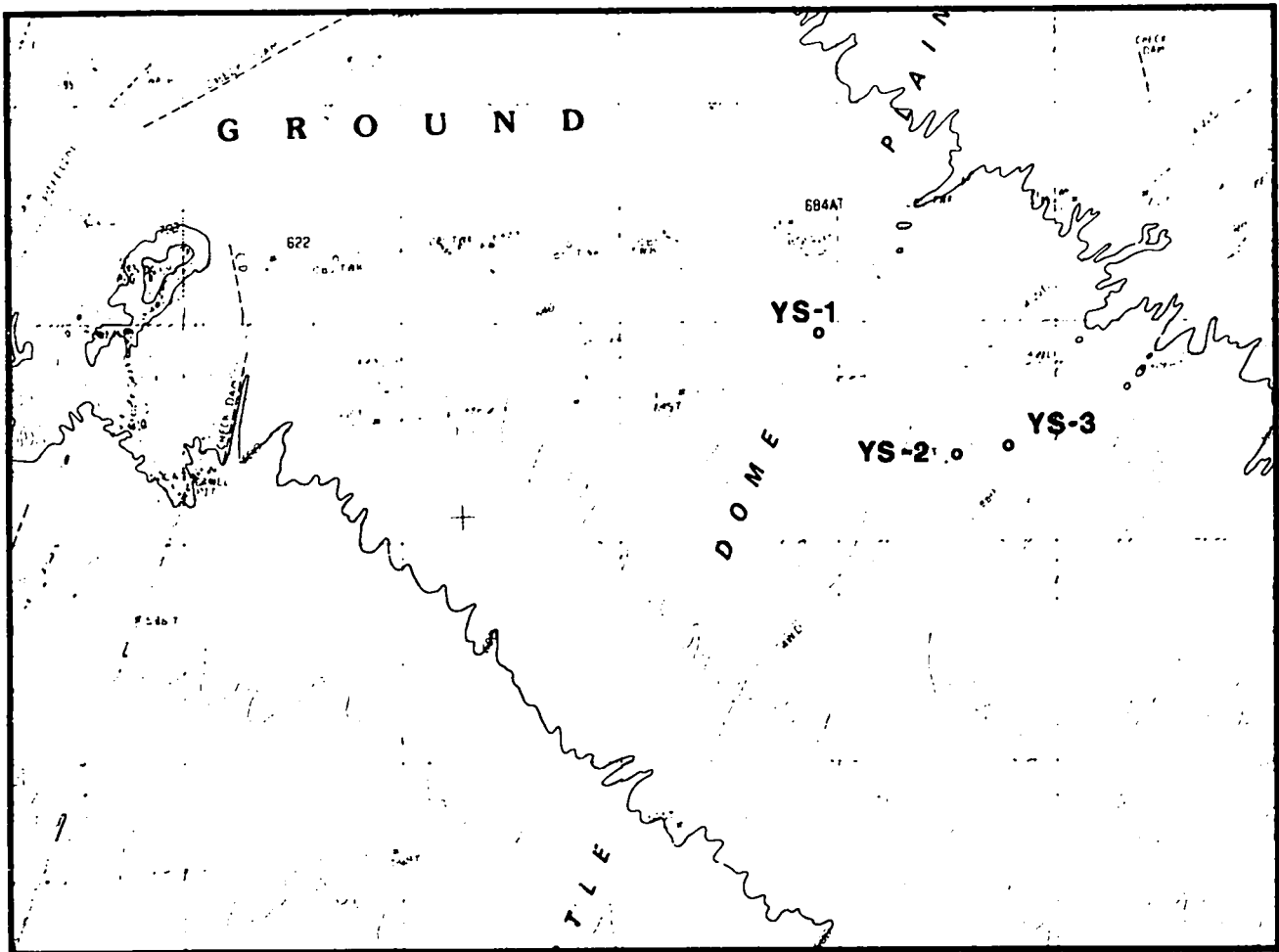Figure 2B. Map of background water sample location, range B-3, APG.

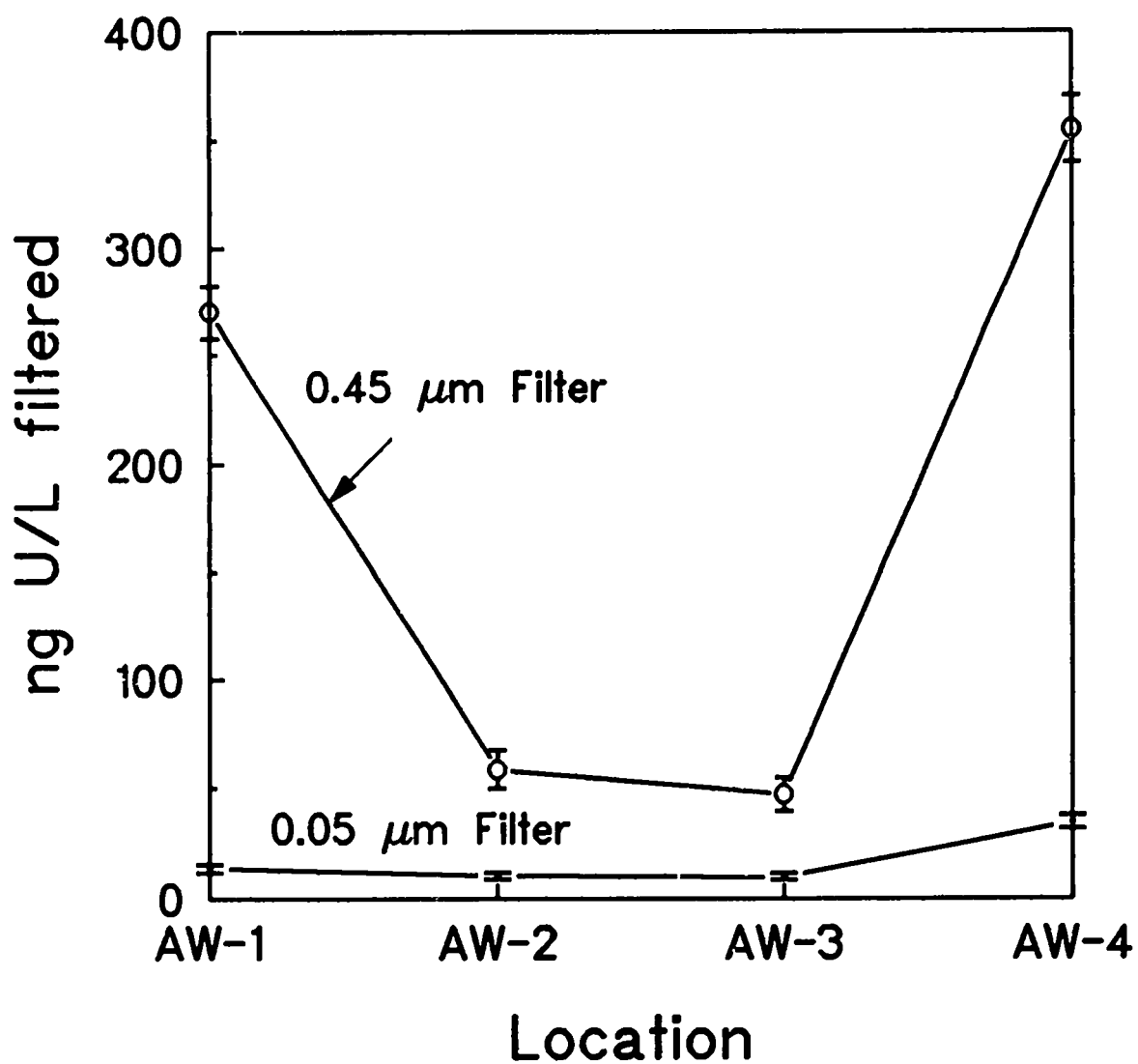Figure 3. Map of soil sampling locations cn Kofa Range, YPG.

Figure 4. Total U on 0.45-μm and 0.05-μm filters, APG water samples. Mean of three measurements plotted. Error bars are standard deviations about the mean.
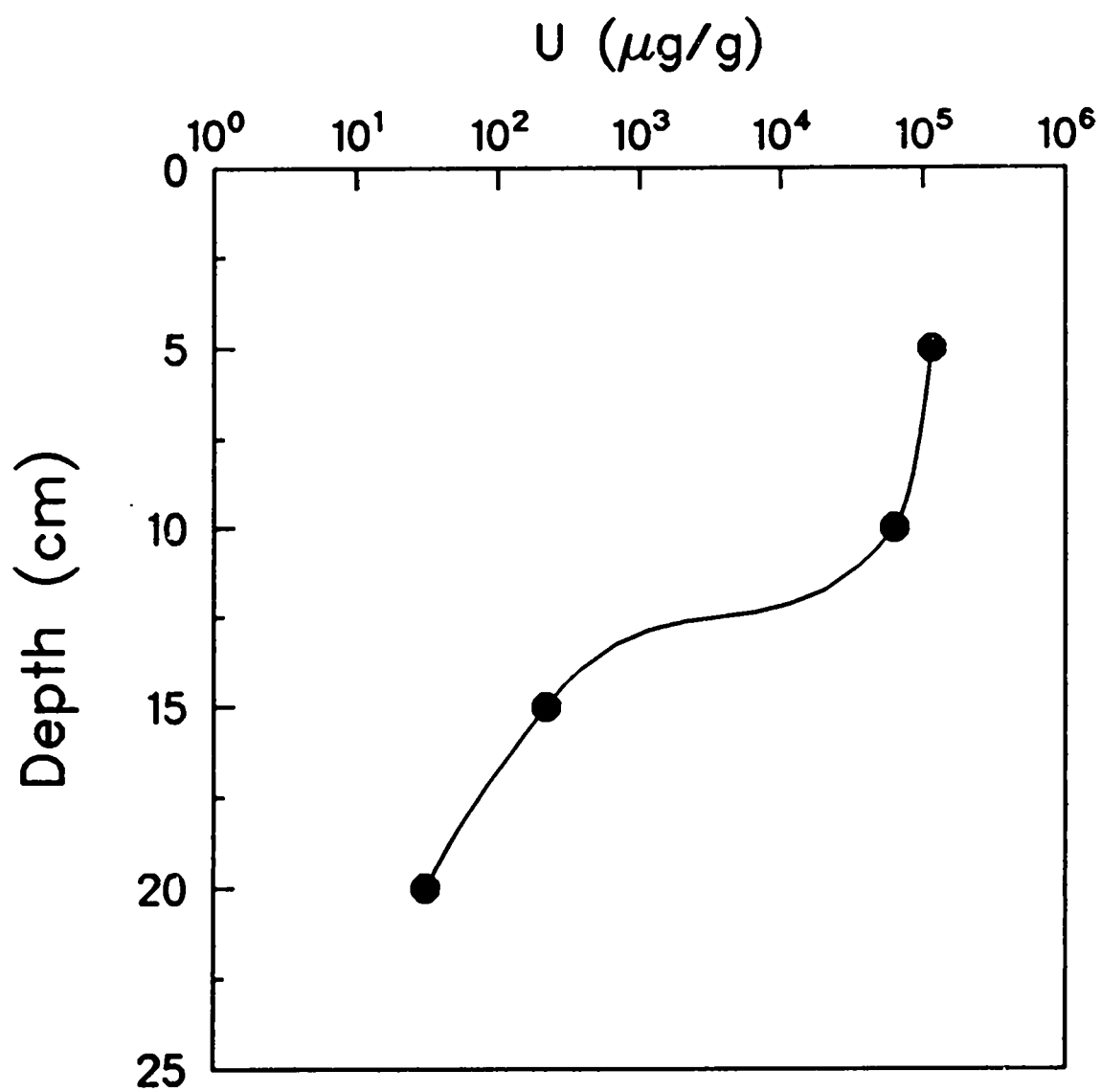
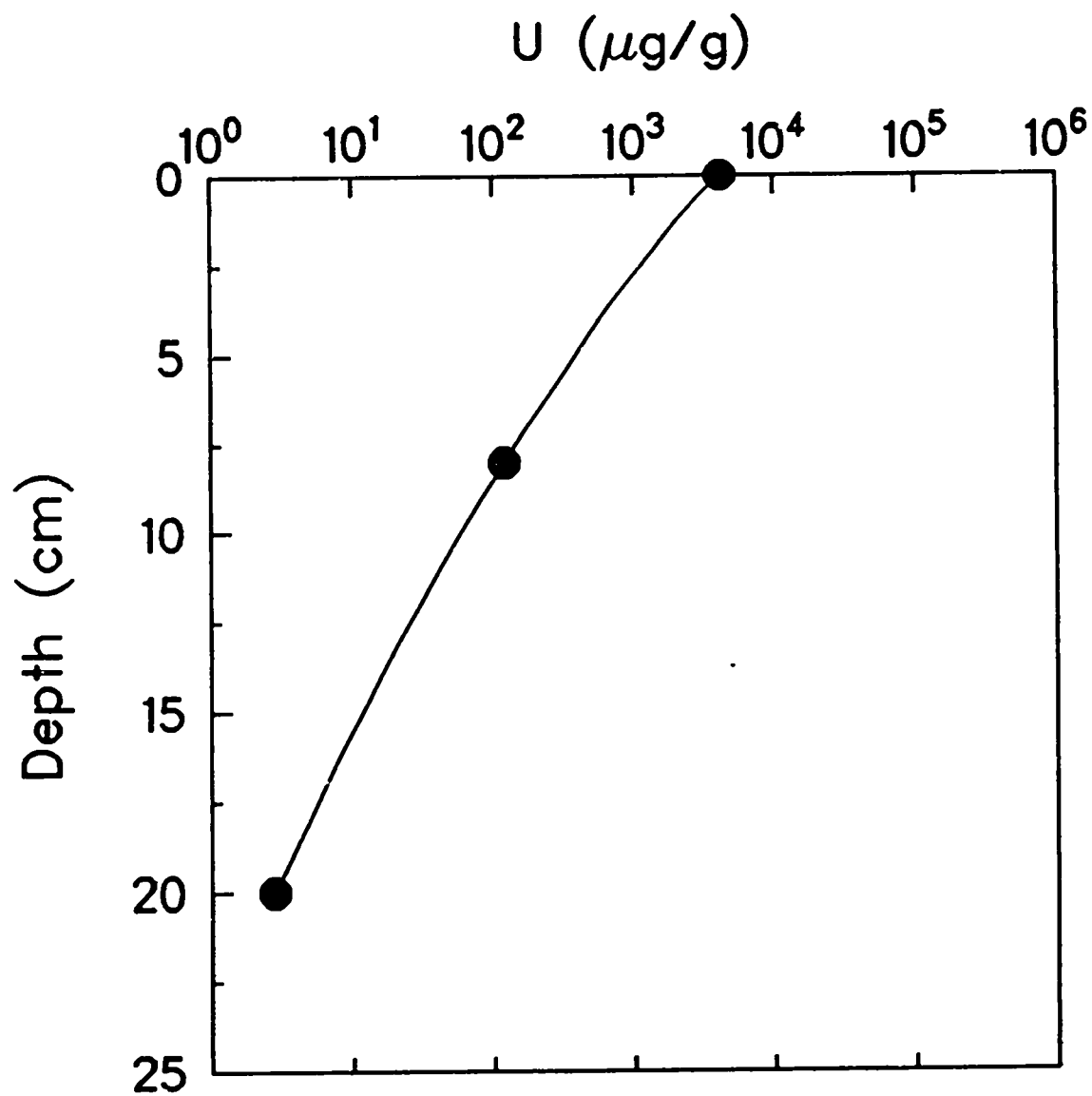Figure 5. Total U with depth in soil profile from location AS-3, APG.

Figure 6. Total U with depth in soil profile from location YS-3, YPG.

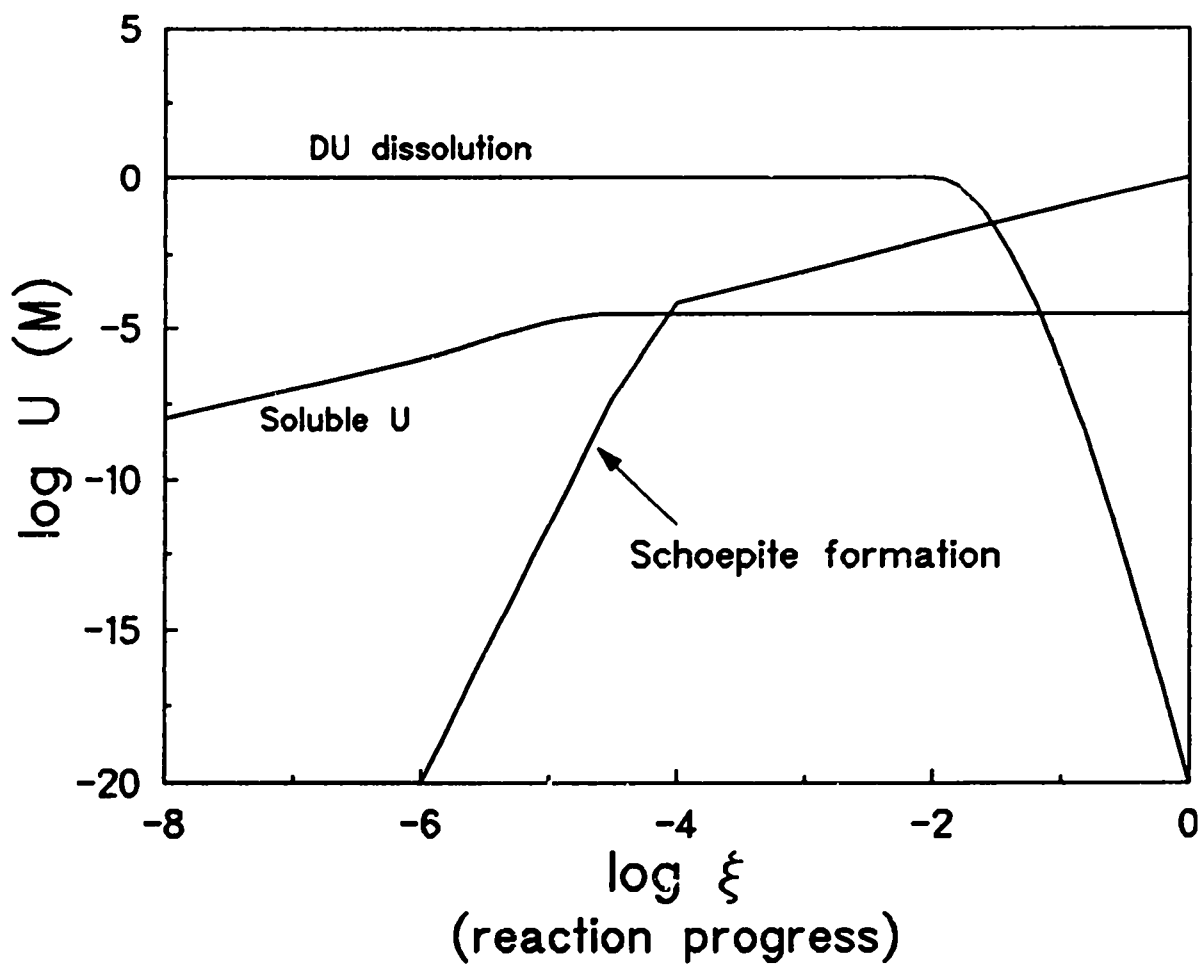Figure 7. Calculated DU dissolution in pure water. Reaction progress (ξ) is the number of moles of solid DU dissolved.
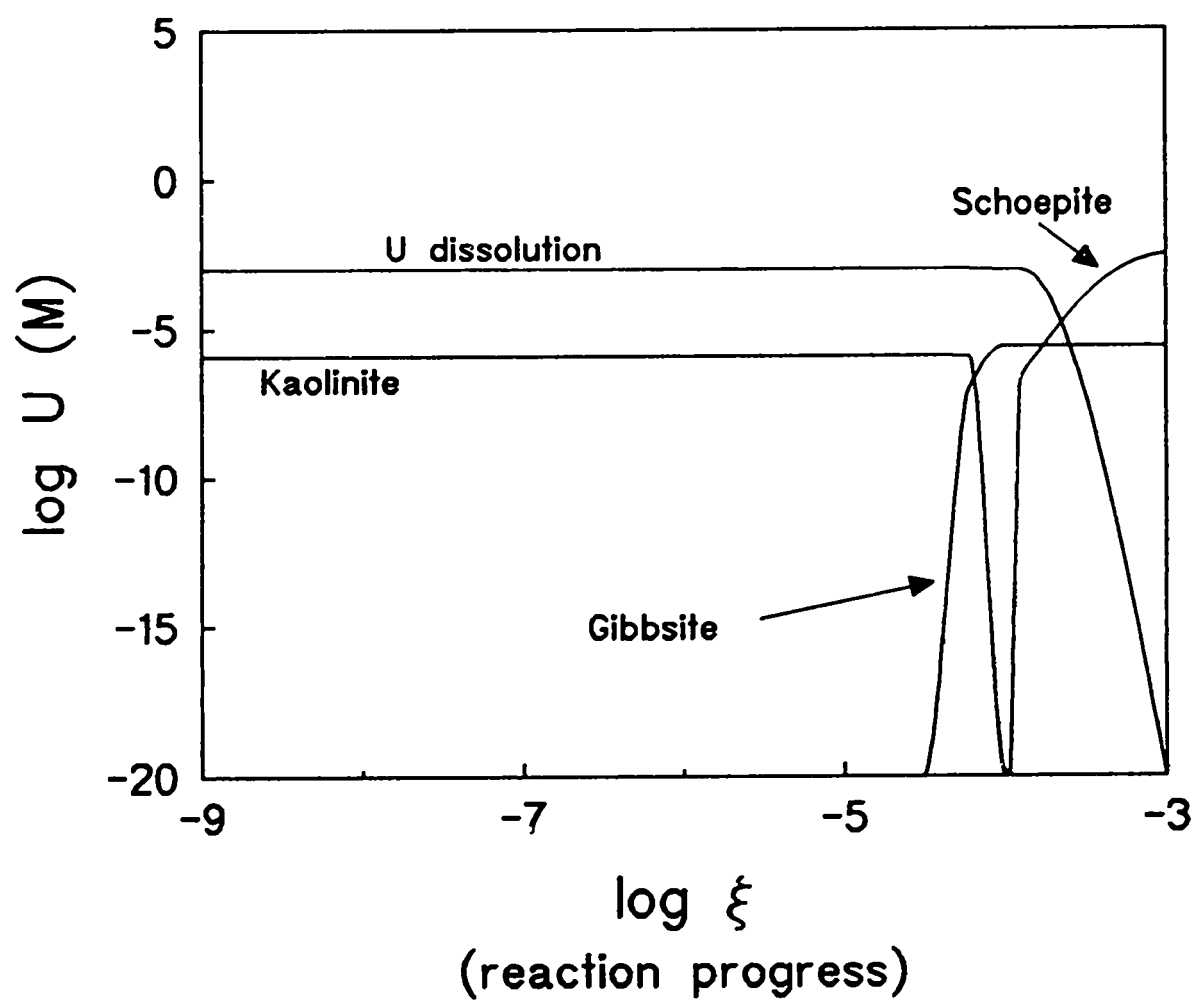
Figure 8. Calculated DU dissolution in water from APG. Reaction progress (ξ) is the number of moles of solid DU dissolved.
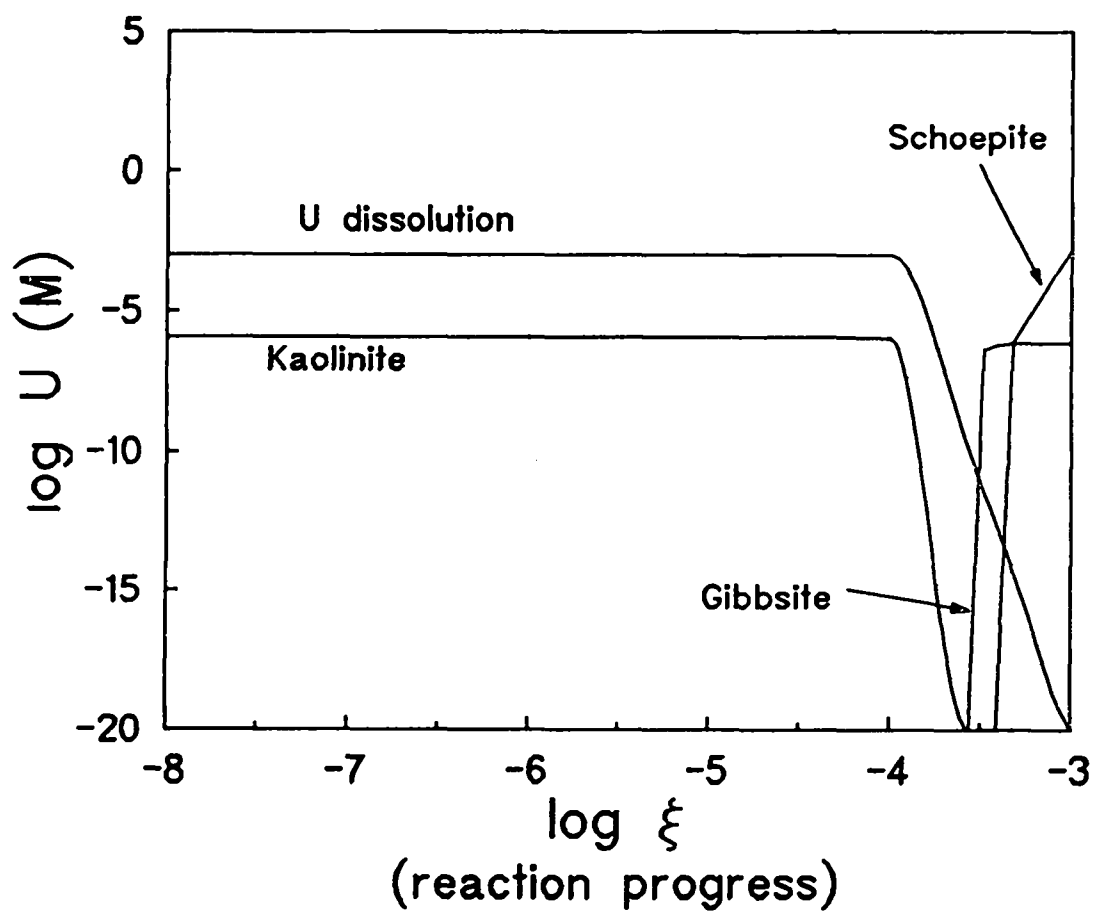
Figure 9. Calculated DU dissolution in water from YPG. Reaction progress (ξ) is the number of moles of solid DU dissolved.

Figure 10. Uranium solubility vs. pH. U(VI) concentration controlled by
tyuyamunite, U(IV) concentration controlled by uraninite.

Figure 11.   Calculated U transport in saturated soil.   Dispersivity (D) = 10
m^2/d, water flow velocity (v) 1 m/d, distance from source (x) is
100 m.   Simulations were made for 1000 d, but only 650 days shown.

Table 1. Description of samples collected from APF and YPG by Los Alamos
National Laboratory in May and June, 1989.

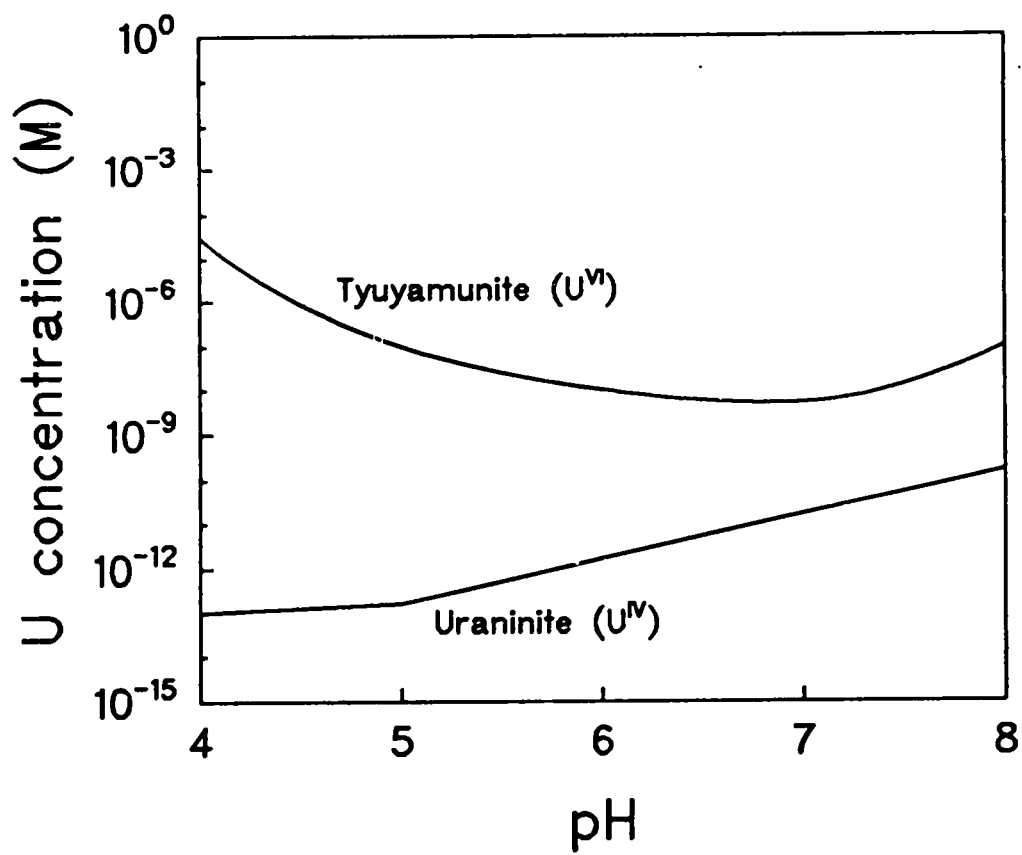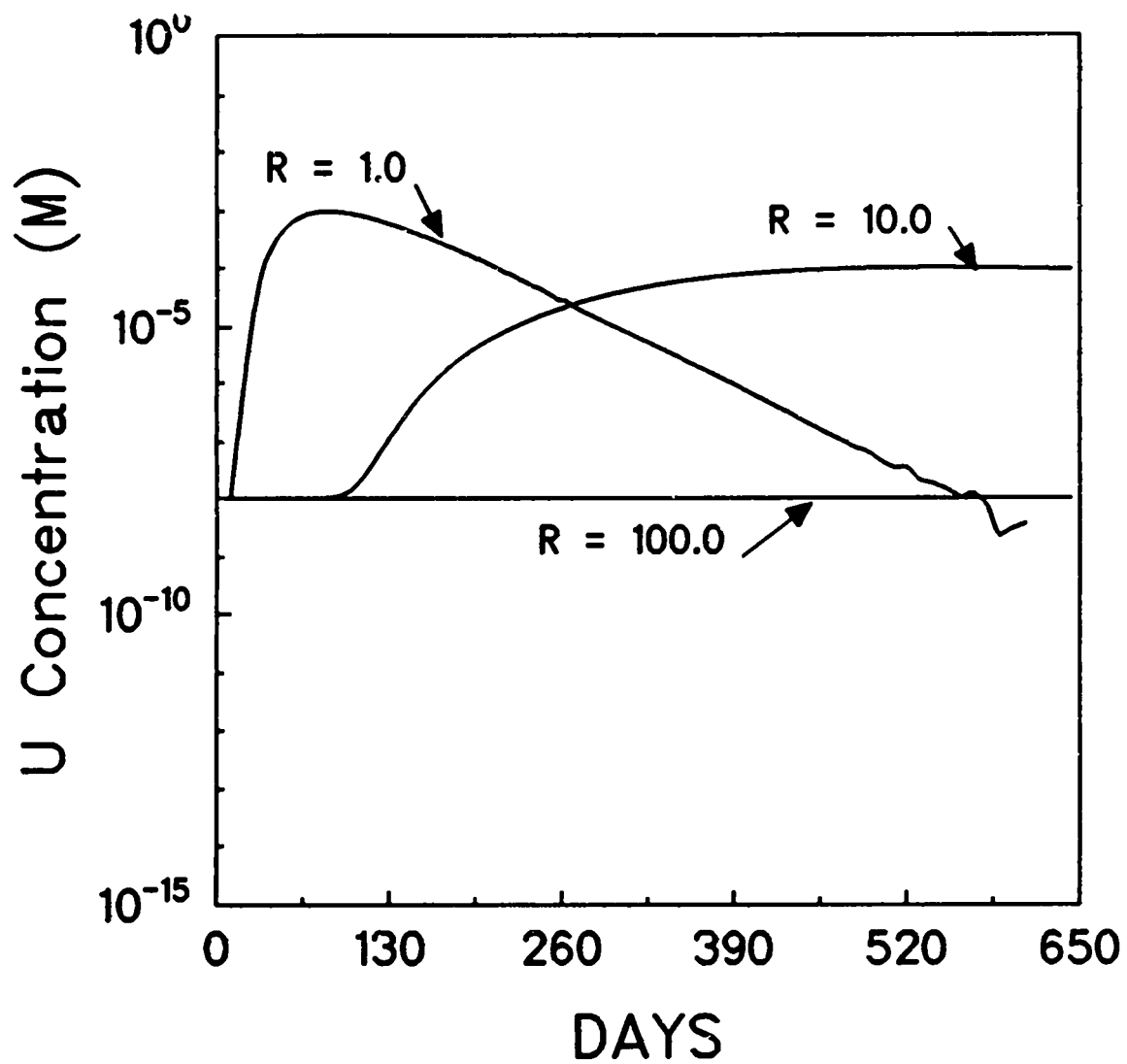APG (see Figures 2A and 2B)

Soil

AS-1   Background sample located in forest just north of 4-km target on
        range B-3.

AS-2   About 5.4 km from gun positions on range B-3; AS-2 penetrator
        buried vertically 0-10 cm from surface;

AS-3   Penetrator lying horizontally on surface

Water

AW-1   Mosquito Creek near 4 km target on range B-3

AW-2   Romney Creek near drop tower entrance on Michaelsville Road
        (background sample)

AW-3   Near mouth of Mosquito Creek into Chesapeake Bay (brackish)

AW-4   Small pond 5.4 km from gun position on range B-3

Sediment

AD-1   Same as AW-1

AD-2   Same as AW-2

AD-3   Same as AW-3

AD-4   Same as AW-4

Yuma (see Figure 3)

Soil

YS-1   North of Kofa firing range on Mortar Range Road about 3 km east of
        GP20 (background sample)

YS-2   Stream channel sediment taken 30 m west of impact area located 4
        km east of GP 20

YS-3   Impact area 4 km east of GP 20 (penetrator impact area)

Water

YW-2   Collected from well H

Sediments
        None collected

Table 2. Results of chemical analyses of waters from YPG (sample YW-2) and APG (samples AW-1 - AW-4). Units are mg/L, and uncertainty is within 10% unless indicated in parentheses.

Element	YW-2	AW-1	AW-2	AW-3	AW-4
Mg	0.3	2.0	2.0	7.0	0.8
Ca	23.0	4.0	5.0	11.0	2.0
Na	350.0	6.0	2.0	30.0	2.0
K	5.0	0.4	0.4	3.0	3.0
Al	<0.07	<0.07	<0.07	<0.07	0.4
Si	20.0	9.0	0.7	2.0	0.5
Fe	0.06	0.4	3.0	0.3	1.0
Cl	694.0	3.9	2.1	44.5	2.5
F	9.2	<0.2	<0.2	<0.2	<0.2
NO_3-N	0.7	<0.2	0.4	<0.2	<0.2
PO_4-P	0.2 (0.2)	<0.2	<0.2	<0.2	<0.2
SO_4	369.0	4.5	2.8	32.8	8.0
Alk.[a]	1.4×10^{-3}	4.2×10^{-4}	2.4×10^{-4}	5.6×10^{-4}	$<10^{-6}$
pH	8.13	6.37	6.17	7.04	5.12
DO[b]	4.55	5.0	2.1	5.9	3.3
TOC[c]	24	7	20	17	14
U_{total}	<d.l.[d]	<d.l.	<d.l.	<d.l.	<d.l.
$^{235}U/^{238}U$	---[e]	---	---	---	---

[a] Total alkalinity, meq/ml, by titration.
[b] Dissolved Oxygen, mg/l.
[c] Total Organic Carbon.
[d] Detection limit was 1.0 x 10-3
[e] No U^{235} present in samples.

Table 3. Total uranium from filters used to filter water samples, units are ng U/L water filtered.

Sample	U_{Total} 0.45 μm filter	0.05 μm filter
YW-2	38	14
AW-1	270	14
AW-2	59	11
AW-3	48	10
AW-4	355	35

Table 4. Total uranium and isotope data from APG soils and sediments. AS-1 was the control (background) sample at the 4000 m target, AS-2 was from penetrator fragment buried vertically in the soil approximately 1500 m from the 4000 m target, and AS-3 was from penetrator impact on the soil surface approximately 20 m from AS-2. AD-1 - AD-4 correspond to locations of water samples. Units are μg-U/g-soil, values are means of triplicate measurements, and values in parentheses are standard deviations of the means.

Sample	Depth (cm)	U_{Total}	$^{235}U/^{238}U^a$
AS-1A	0-5	6.3 (1.3)	0.0053
AS-1B	5-15	2.5 (0.8)	0.0073
AS-1C	15-23	3.4 (0.9)	0.0029
AS-2A	0-10[b]	38,000 (5000)	0.0019
AS-3A	0-5	115,000 (12,000)	0.0022
AS-3B	5-10	63,000 (8,300)	0.0022
AS-3C	10-15	220 (30)	0.0020
AS-3D	15-20	31 (15)	0.0021
AD-1	N/A[c]	2.3 (0.7)	0.0036
AD-2	N/A	4.4 (2)	0.0073
AD-3	N/A	<1	0.0027
AD-4	N/A	<1	0.0048

[a] $^{235}U/^{238}U$ > 0.0065 indicates natural U, <0.0065 indicates U from DU.
[b] Single integrated sample from 0 to 10 cm.
[c] Not applicable; samples collected from top of sediment.

Table 5. Total uranium and isotope data from YPG soils. YS-1 was control (background) sample, YS-2 was in wash adjacent to impact area, and YS-3 was in impact area. Units are μg-U/g-soil, values are means of triplicate measurements, and standard deviations of the means are reported in parentheses.

Sample	Depth (cm)	U_{Total}	$^{235}U/^{238}U$ [a]
YS-1A	0-20	2.8 (0.3)	0.0076
YS-1B	20 60	3.5 (1.1)	0.0078
YS-1C	60-90	2.3 (0.3)	0.0072
YS-1D	90 +	1.8 (0.4)	0.0075
YS-2A	0-20	310 (27)	0.0019
YS-2B	20-30	197 (6)	0.0021
YS-3A	Surface	4230 (320)	0.0023
YS-3B	1-8	121 (38)	0.0020
YS-3C	8-20	2.8 (0.3)	0.0071

[a] $^{235}U/^{238}U$ > 0.0065 indicates natural U, <0.0065 indicates U from DU.

37